Regeneration of Ammonia Borane Spent Fuel(s) by Direct Reaction with Hydrazine and Liquid Ammonia

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What Does H_2 Offer as an Alternative Fuel?

- Potentially part of a renewable energy cycle

- Water is the sole oxidation product

$$2H_2 + O_2 \longrightarrow 2H_2O$$

- Favorable energy content per kg (120 MJ) compared to petroleum (44 MJ)

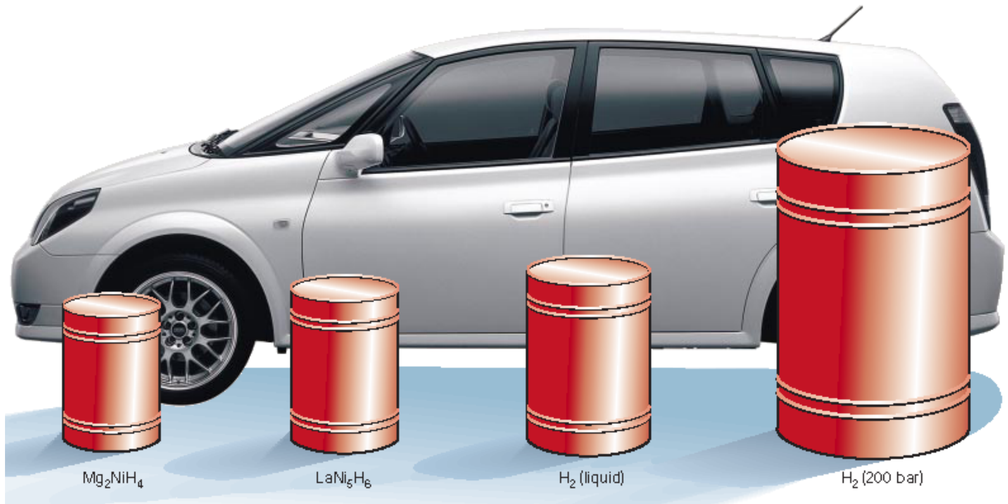
(corresponds to ~19 MJ/L for AB (Based on $3H_2$ released) versus ~34MJ/L for gasoline)

- Can be used in a PEM fuel cell

How Can H_2 be Stored in a Vehicle?

- Physical
  - As a compressed gas at high pressure
  - As a liquid, cryogenically
  - Using sorbants (nanoporous materials)
- Chemical
  - Metal hydrides
  - Chemical hydrides

DOE Volumetric and Gravimetric Targets[1]

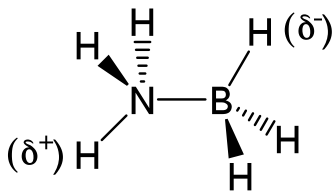


Relative volumes of 4 kg of H_2[2]

	2010	2015	Ultimate
Gravimetric (wt. %)	4.5	5.5	7.5
Volumetric (MJ/L)	3.2	4.7	8.3

[1]http://www1.eere.energy.gov/hydrogenandfuelcells/storage/pdfs/targets_onboard_hydro_storage.pdf
[2]Schlapbach, L.; Zuettel, A. *Nature* ***2001,*** *414,* 353-358.

Why Ammonia Borane?



Ammonia Borane (AB)

- Advantages
  - Non-toxic
  - Hydridic and protic hydrogen atoms
  - High wt. % of hydrogen (6.5/13.1/19.6)
- Challenges
  - Controlled Dehydrogenation
  - Regeneration

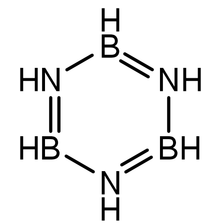
Methods of Dehydrogenation

Insoluble aminoborane

$(H_2NBH_2)_n$

1 eq. H_2 lost

borazine



2 eq. H_2 lost

Borazine (trace in ILs)
Insoluble BNH_x products

Dehydro-oligomerization

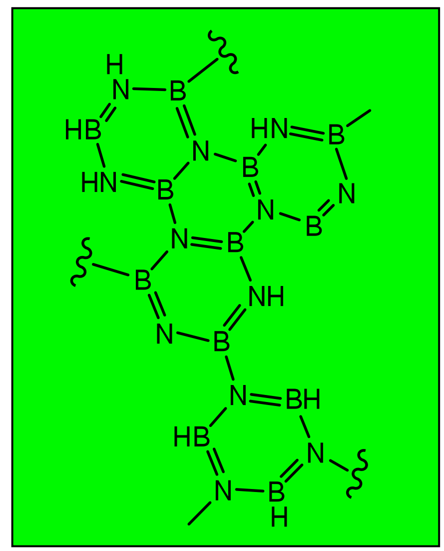
AB

Metal-Based Catalysis

Thermolysis (solution or solid state)

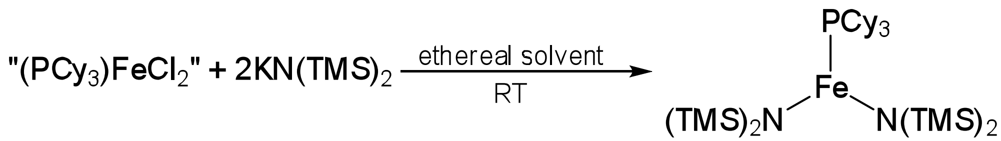
Polyaminoboranes (1 eq. H_2 loss)
Polyiminoboranes (1 eq. H_2 loss)
Borazine (except nanomaterials)

Soluble Polyborazylene

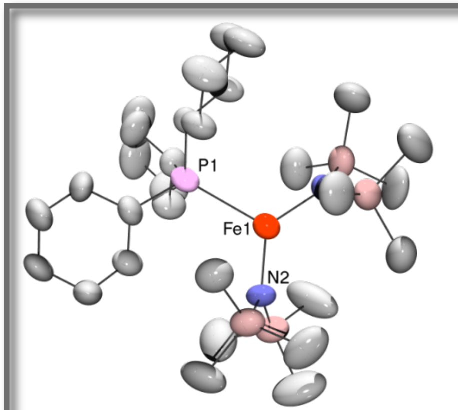


> 2 equiv H_2 lost

Earth Abundant Catalyst Development



Colorless solid, *ca.* 18 % purified yield
Cy = Cyclohexyl, TMS = Trimethylsilyl

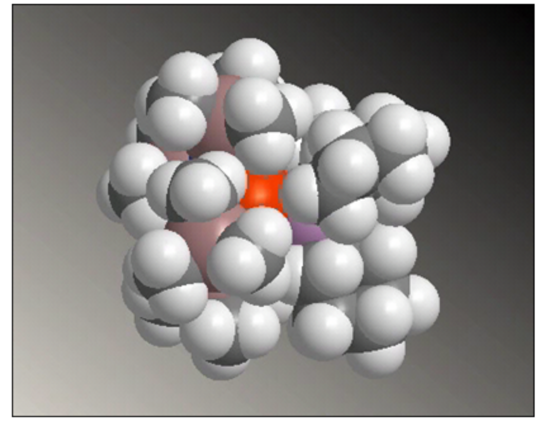


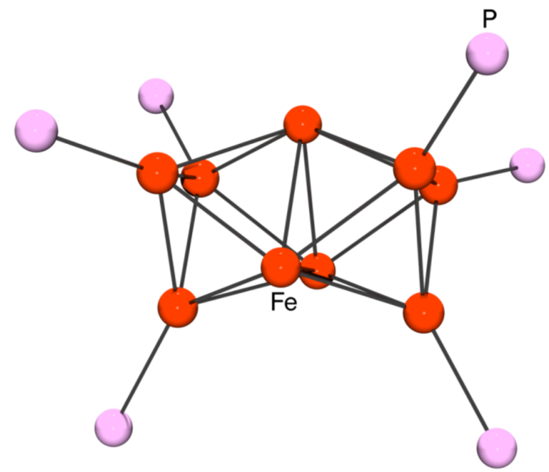
Thermal ellipsoids at 50% probability with hydrogen atoms omitted.

$P2_1/n$	
R_1	7.4 %
	(Å)
Fe(1)-P(1)	2.619(4)
Fe(1)-N(1)	1.927(10)
Fe(1)-N(2)	1.932(8)
	(°)
P(1)-Fe(1)-N(1)	116.3(3)
N(1)-Fe(1)-N(2)	127.9(4)
N(2)-Fe(1)-P(1)	115.8(3)
N(1)-N(2)-P(1)-Fe(1)	~1

$$\text{AB} \xrightarrow[\Delta]{} (\text{NH}_2\text{BH}_2)_n + (\text{NHBH})_n$$

- Mixture of products
    - Depends on rxn. conditions
- 2.5 – 3 h reaction time
- *ca.* 3.5 mol. % catalyst loading
- 1.5 – 1.7 eq. H_2 per AB
- Very sensitive to oxidation/decomp.
- Trigonal planar coordination geom.





$PCy_3Fe[N(TMS)_2]_2$ + AB in THF at RT. $P6_3$, R1 = 11.5 %, 50 % thermal ellipsoids, cyclohexyl P substituents omitted.

Baker, Gordon, Hamilton, Henson, Smythe

Los Alamos NATIONAL LABORATORY EST. 1943

Off-Board Regeneration Required

3 Ammonia Borane ($H_3N\text{-}BH_3$) $\rightarrow$ Spent fuel ($B_3N_3H_4$) + $7H_2\uparrow$

$\Delta H \approx$ -7 kcal/mol

(Miranda and Ceder 2007)

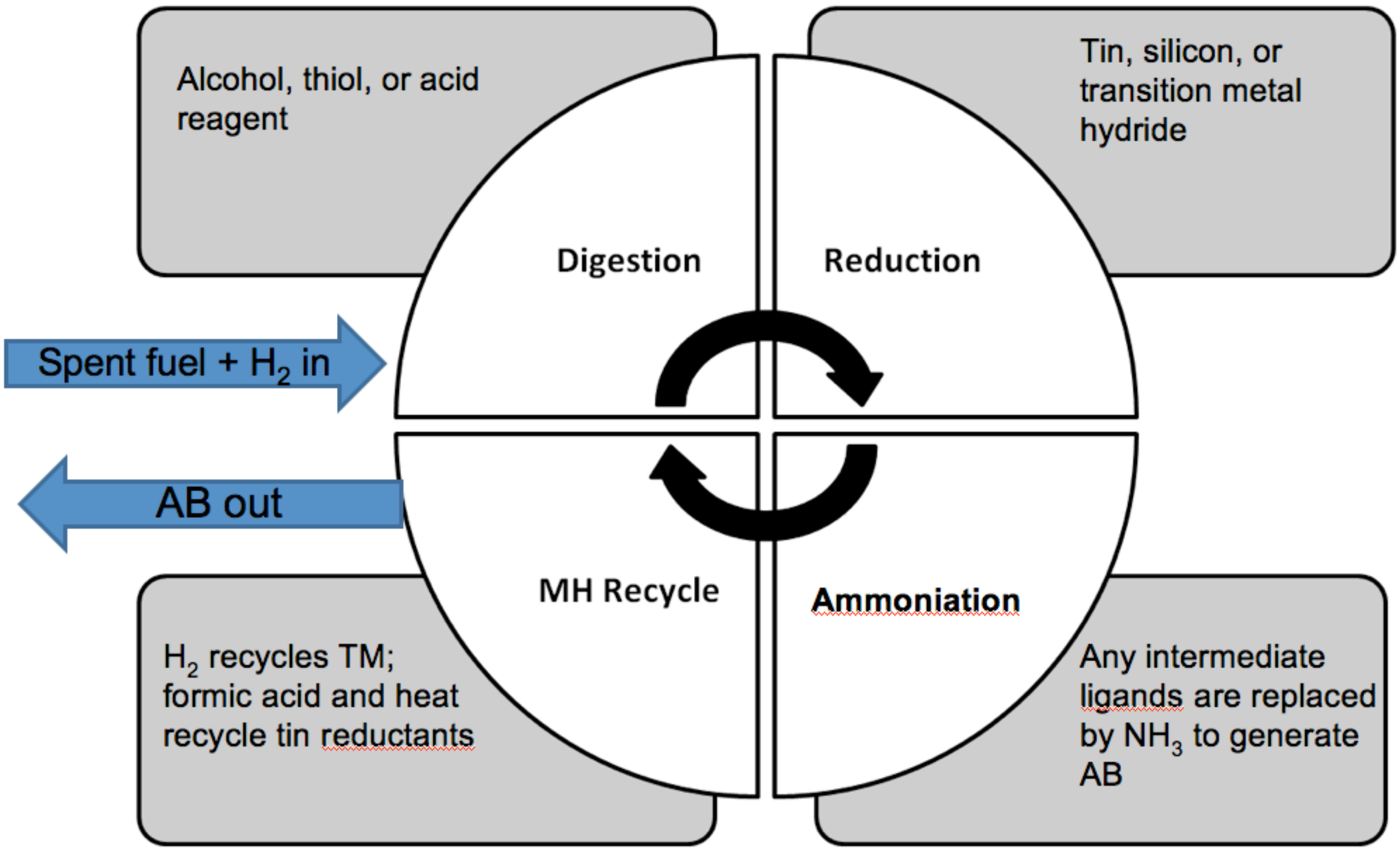
Hydrogen release -> **too exothermic** to merely re-pressurize with H_2

Off-board chemistry required to regenerate ammonia borane (AB)

N.B. Within the Center we are working on systems that are potentially directly regenerable (on-board??):

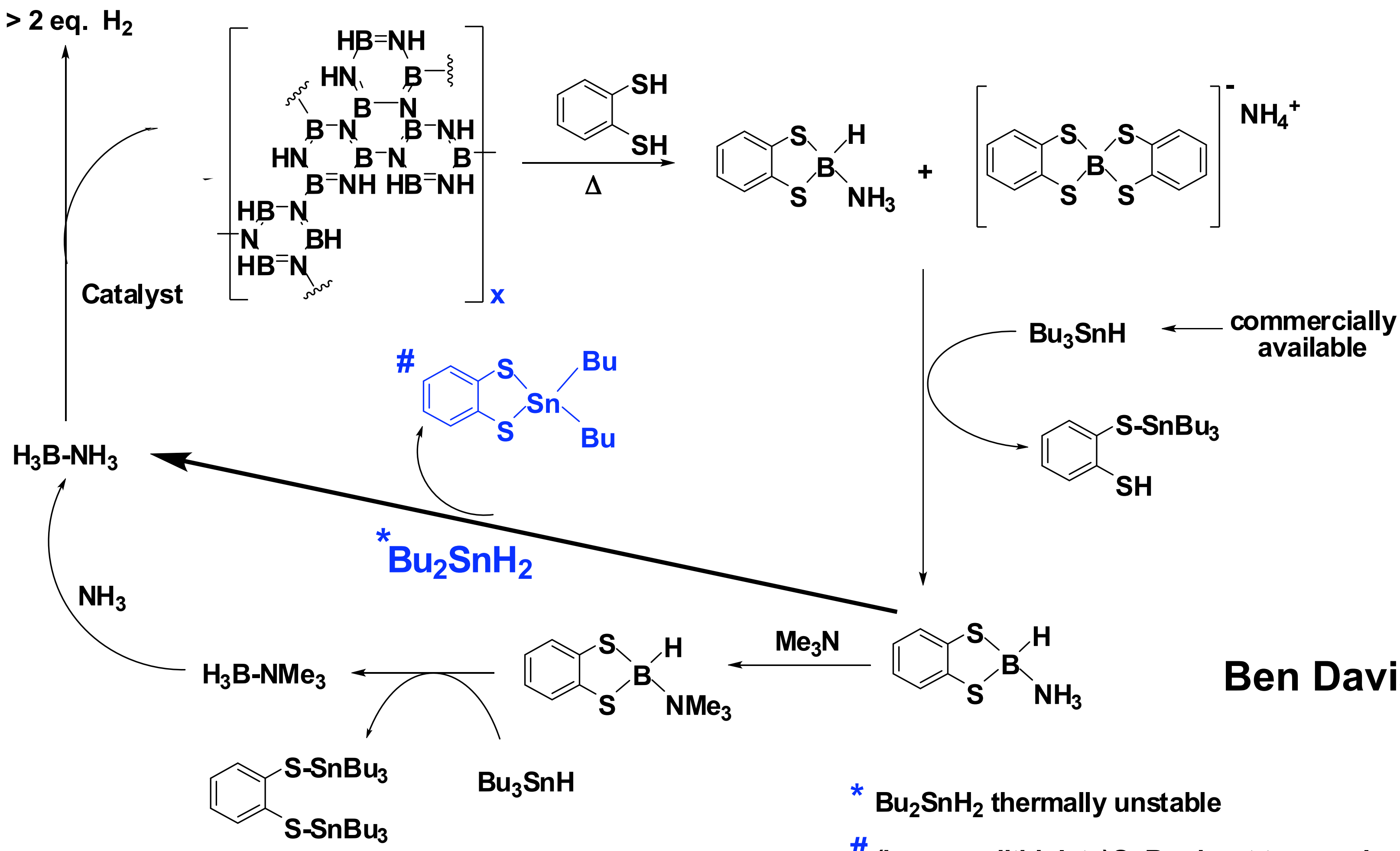
e.g. $Ca(NH_2BH_3)_2$ (A.K. Burrell et. al. *Angew. Chem. Int. Ed*. **2007**, *46*, 8995).

Regeneration Strategy



D. Thorn, B. Davis LANL

Benzenedithiol Chemistry Works with Borazine and PB…



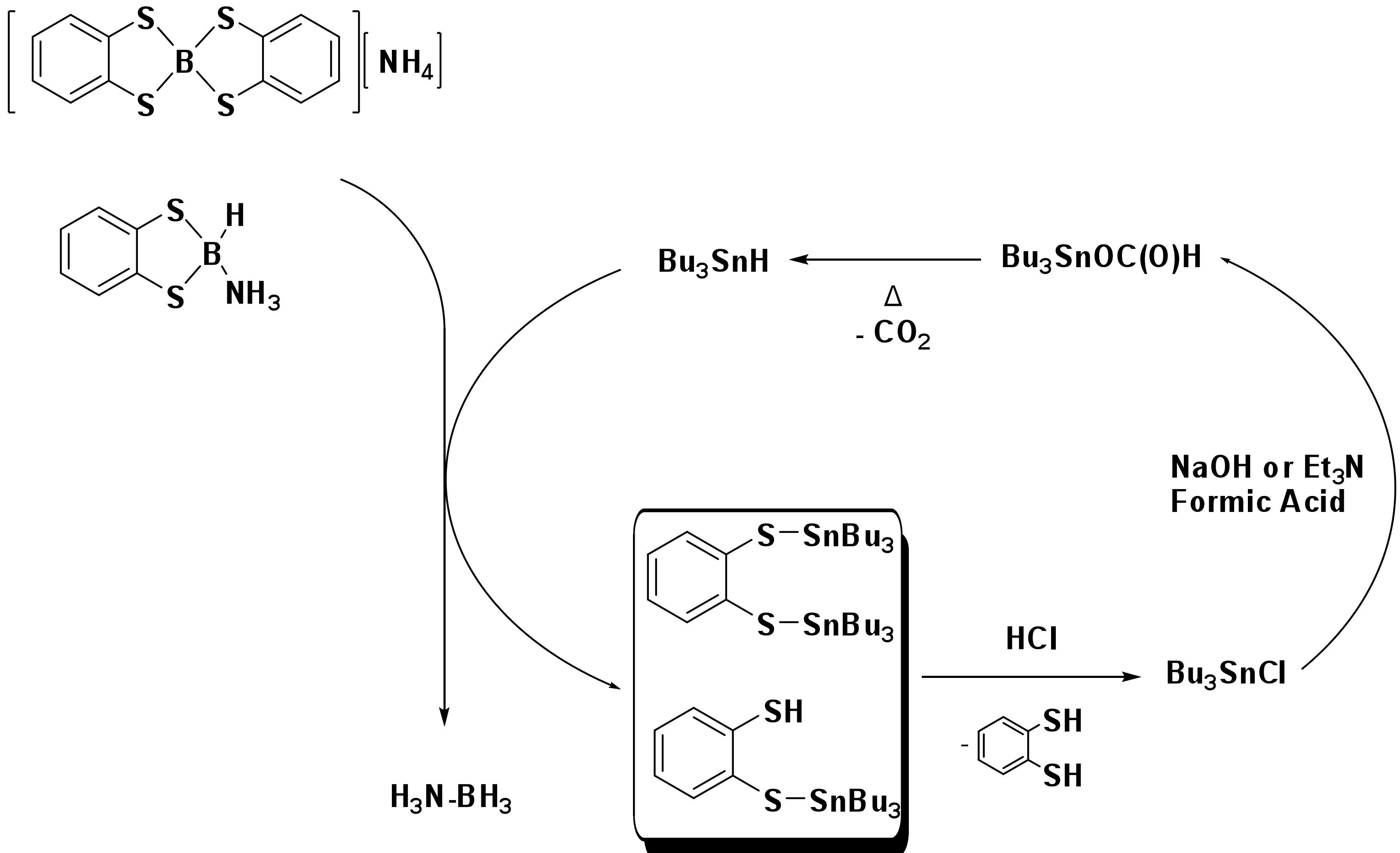
Ben Davis

* Bu_2SnH_2 thermally unstable

\# (benzenedithiolate)$SnBu_2$ inert to recycle

Davis, Dixon, Garner, Gordon, Matus, Scott, Stephens, *Angew. Chem. Int. Ed.*, **2009**, *48*, 6812.

Sn-H Recycle from Sn-S is Also Required…



Sutton, Davis, Bhattacharyya, Ellis, Power, Gordon, *Chem. Commun.*, **2010**, *46*, 148.

Drive to Reduce Mass - 100 Metric Ton/Day Recycle of AB……

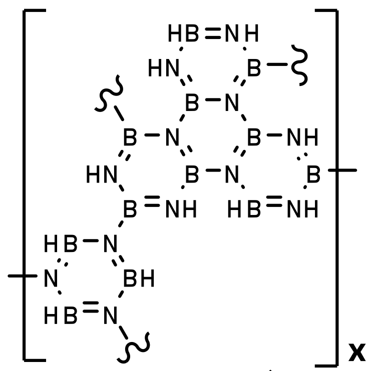
Rohm & Haas Report Detail

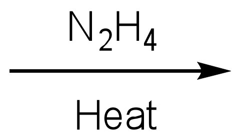
	Digestion	Metal Reduction / Amine Exchange	Ammoniation	Metal Recovery
H_2		431		1,145
NH_3		15,645	3,303	
$(Et)_2NH$		14,930	67,187	
THF	86,989	86,989		
Toluene			88,773	
BNH	5,272			
$C_6H_4(SH)_2$	22,505	2,250		222,795
Bu_3SnH		162,797		906,777
$(Et)_2NHBH_3$		79,896	8,877	
$HB(C_6H_4S_2)NH_3$	69,895	17,258		17,258
$(NH_4)B(C_6H_4S_2)_2$	156,278	17,364		17,364
$HB(C_6H_4S_2)NH(Et)_2$		22,985		22,985
$(C_6H_4)(SH)(SSnBu_3)$		276,252		27,625
$C_6H_4(SSnBu_3)_2$		792,217		79,222
NH_3BH_3			28,354	
Total, kg/hr	**340,938**	**1,489,015**	**196,494**	**1,295,171**

Reduce mass of reducing agent – reduce cost of recycle

Can We Get Away Completely From Tin Use?

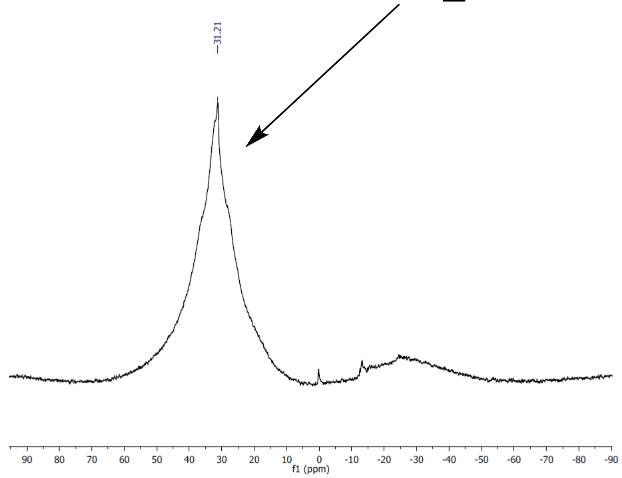
Direct Hydrazine Reduction of PB!

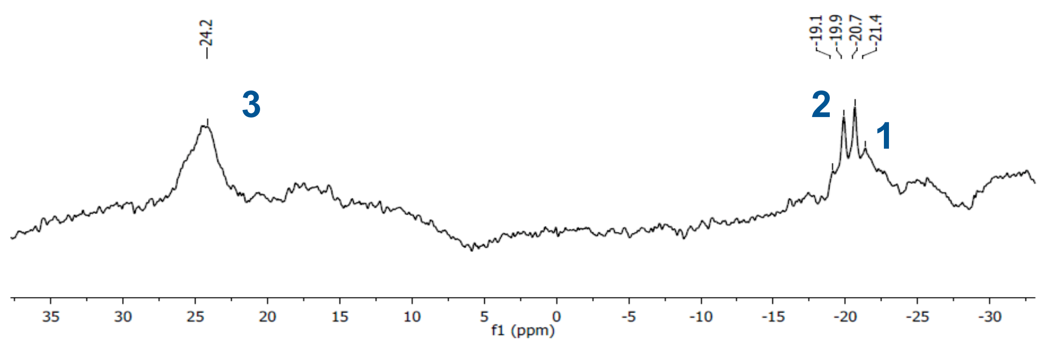




$H_3N\text{-}BH_3$ + $(H_4N_2)\text{-}BH_3$ + "$B(N_2H_3)_3$"

1 — Major Product **2** — **3**





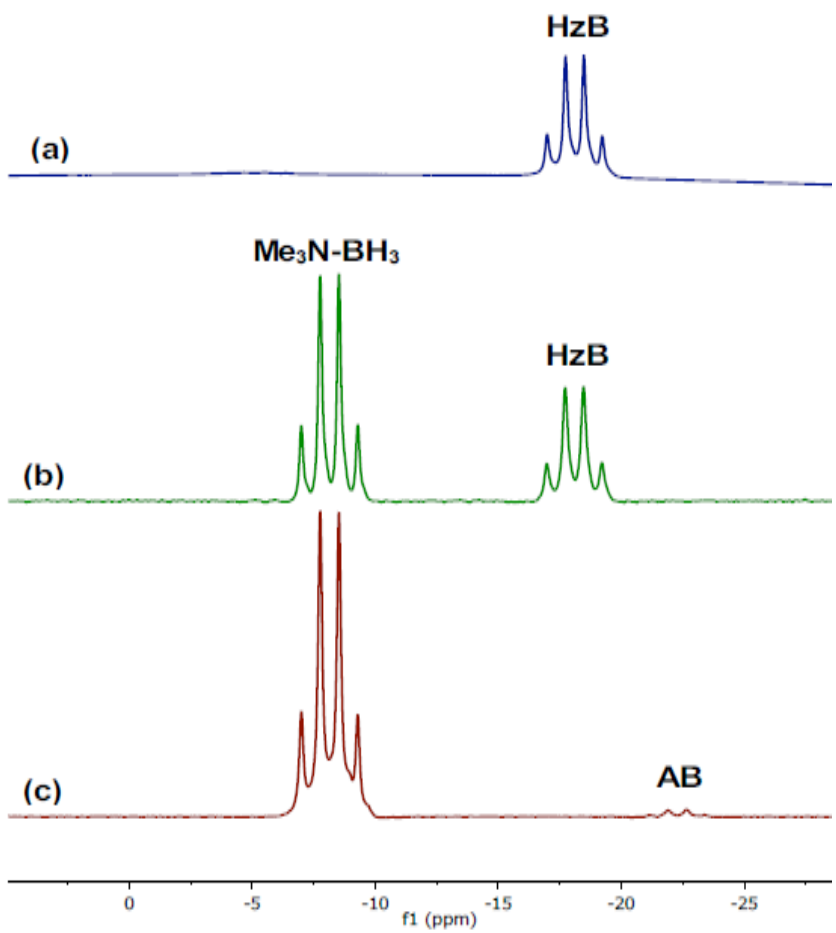
How to Display Hydrazine and Replace with Ammonia?

Hydrazine-BH_3 + R → R-BH_3 + Hydrazine Calculations

Reactant	B3LYP ΔΔH(rel BDE)		G3MP2 ΔΔH(Rel BDE		B3LYP BDE absolute rel to CCSD(T) NH2NH2		G3MP2 BDE absolute rel to CCSD(T) NH2NH2	
	0K	298K	0K	298K	0K	298K	0K	298K
Ph-NH_2	8.0	8.2	7.0	7.3	39.0	40.4	38.0	39.5
$(C_8H_{18})_3N$	3.0	2.9			34.0	35.1		
Et_3N	3.3	3.0	-1.9	-2.0	34.3	35.2	29.1	30.2
Et_2NH	0.8	0.9	-1.5	-1.5	31.8	33.1	29.5	30.7
EtMeNH	-0.7	-0.6	-2.6	-2.5	30.4	31.6	28.4	29.7
Me_3N	-0.9	-0.8	-4.4	-4.4	30.1	31.4	26.6	27.8
Me_2NH	-1.6	-1.5	-3.3	-3.3	29.5	30.7	27.7	28.9
NH_3	4.7	4.4	6.2	5.9	35.7	36.6	37.2	38.1
Me_2S	9.4	9.8	7.8	8.3	40.4	42.0	38.8	40.5
Et_2S	8.8	9.2	6.9	7.4	39.8	41.4	37.9	39.6
Ph_2S	14.4	14.8	12.1	12.7	45.7	47.0	43.1	44.9
Me_2O	14.5	14.7	13.4	13.8	45.5	46.9	44.4	46.0

Dave Dixon, Monica Vasiliu, University of Alabama.

Hydrazine-BH_3 + NMe_3

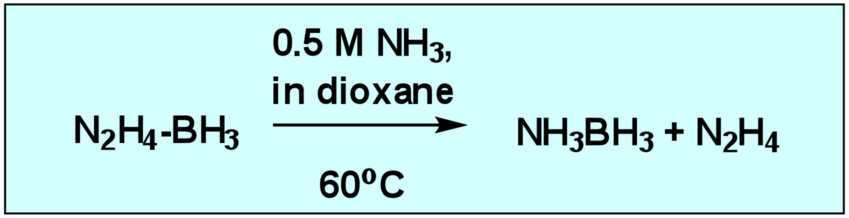


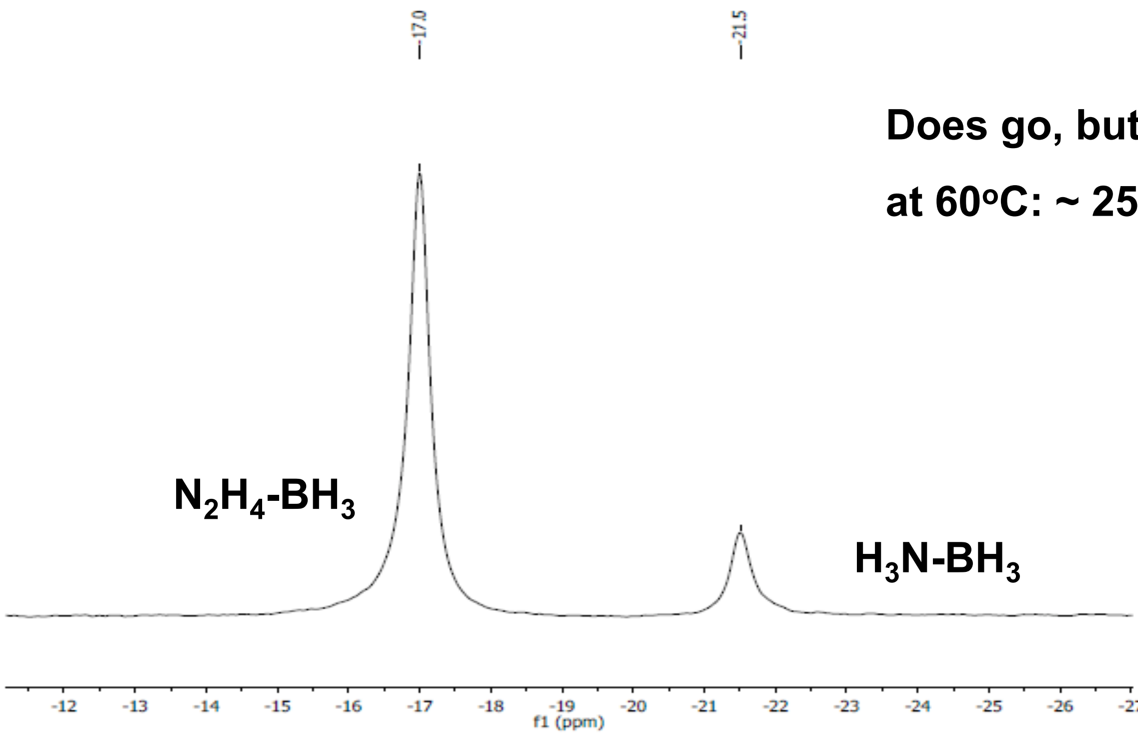
Pure HzB

Reaction of HzB and Me_3N in THF overnight: ~ 60% conversion to Me_3NBH_3

Independently synthesized Me_3NBH_3 with excess NH_3 in THF heated at 50°C for 5 days: < 5 % conversion to AB

What About N_2H_4-BH_3 + NH_3 Directly?

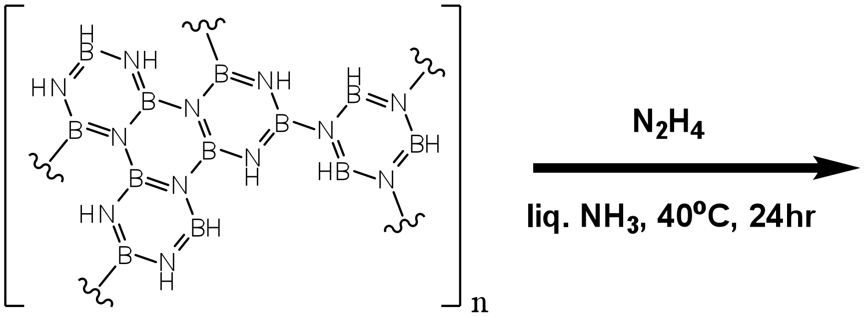


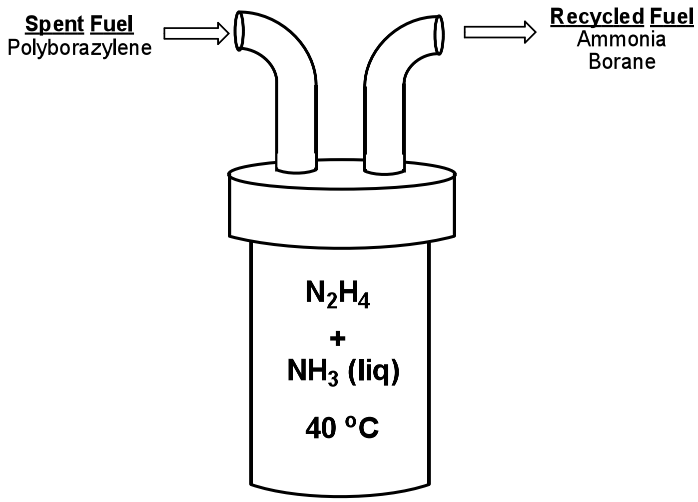


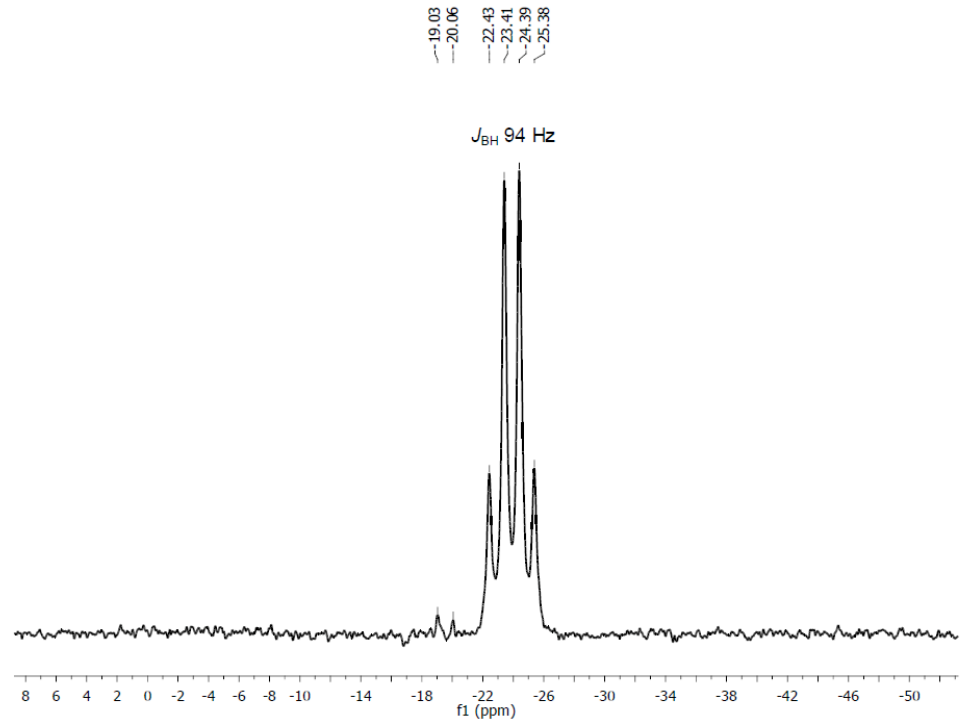
Does go, but requires heat:

at 60°C: ~ 25% conversion….

What About PB + Liq. NH_3 in Sealed (One –Pot) System to Drive Reaction?







^{11}B-NMR spectrum (in THF) of crude material after venting the NH_3

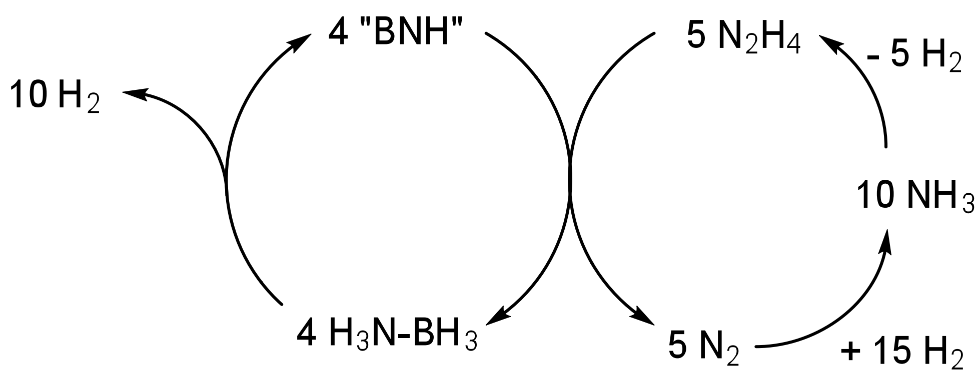
i.e. pressure (~ 211 *psi*) + moderate heat drives the desired rxn.

Can isolate pure samples of AB in > 90% yield using "one–pot" approach…..

***Science*, accepted**

Sutton, Burrell

Summary



"Ideally"
only material consumed would be H_2
(in this case chosen PB = "BNH"
(i. e. 2.5 eq. H_2 released)

At the inception of CHS CoE (~ 5 yrs ago), many "naysayers" thought that regeneration of AB spent fuel was impossible….

Clearly this is not the case…..

Remarkable discoveries have been enabled through Center model of collaboration and sharing of information among interdisciplinary experts

Acknowledgements

Many DOE Chemical Hydrogen Storage Center of Excellence Collaborators

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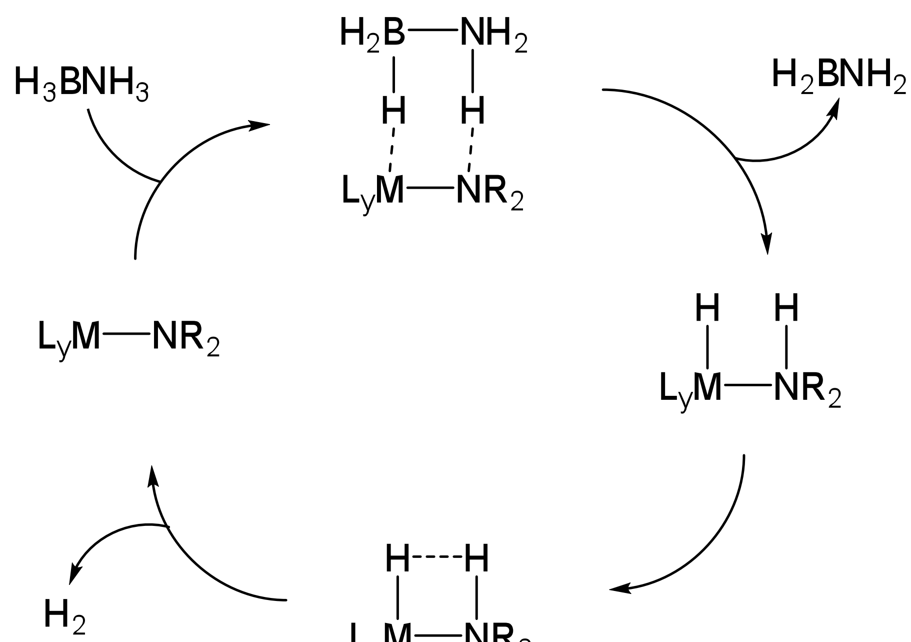
DOE EERE

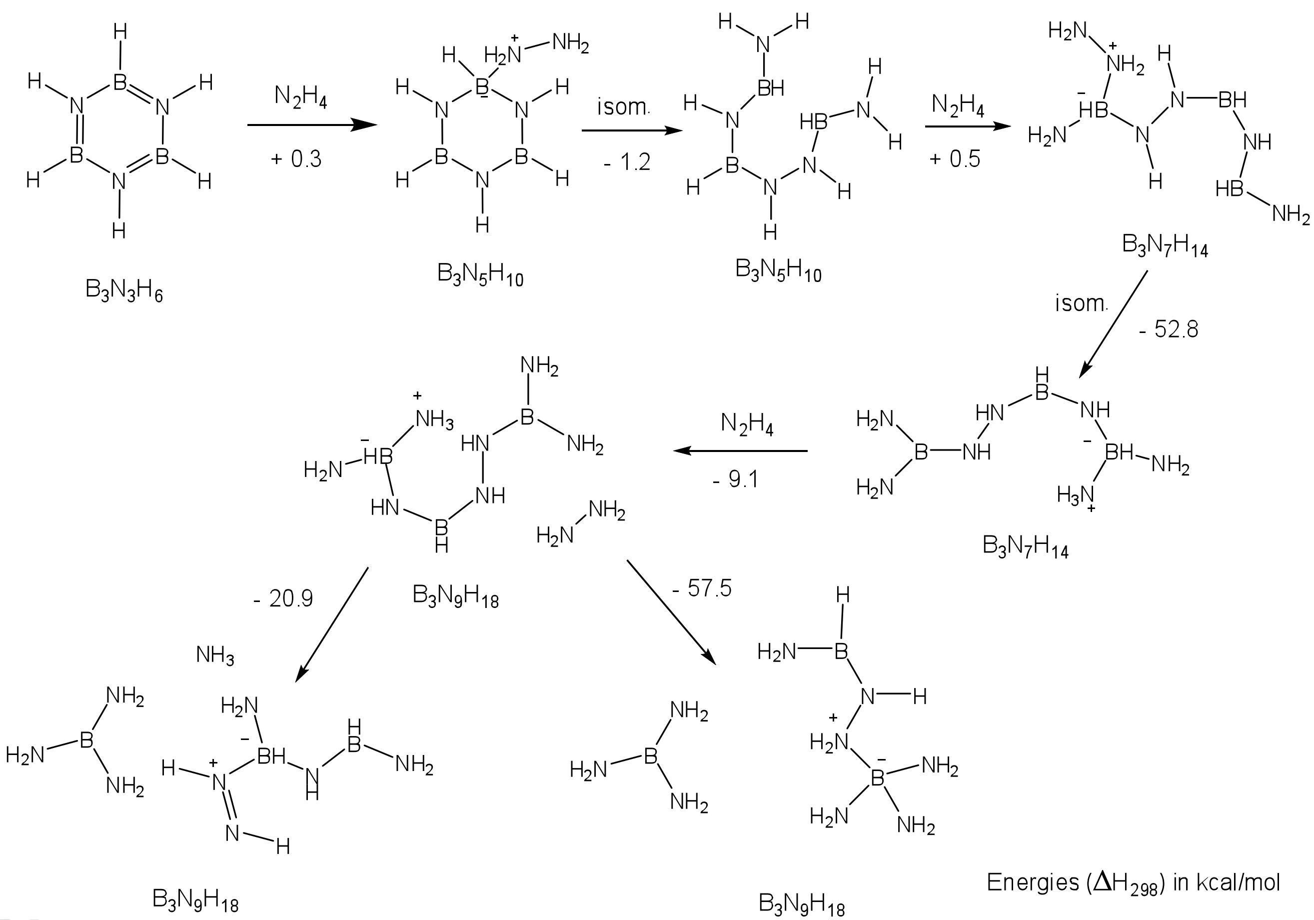
[4+2] Cycloaddition for AB



e.g. Blaquiere, N.; *et al. J. Amer. Chem. Soc.* **2008**, *130*, 14034.

How Does This Work? Some Insight From Theory..

***cyclo*-$B_3N_3H_6$ (i.e."BNH_2") used as a model fragment i.e. loss of 2 eq. H_2 from AB**
***Complicated* - many intermediates (only some shown..) on addition(s) of N_2H_4**



Energies (ΔH_{298}) in kcal/mol

DFT/G3MP2B3